



Synergistically creating sulfur vacancies in semimetal-supported amorphous MoS₂ for efficient hydrogen evolution

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ABSTRACT

The presence of elemental vacancies in materials are inevitable according to statistical thermodynamics, which will decide the chemical and physical properties of the investigated system. However, the controlled manipulation of vacancies for specific applications is a challenge. Here we report a facile method for creating large concentrations of S vacancies in the inert basal plane of MoS₂ supported on semimetal CoMoP₂. With a small applied potential, S atoms can be removed in the form of H₂S due to the optimized free energy of formation. The existence of vacancies favors electron injection from the electrode to the active site by decreasing the contact resistance. As a consequence, the catalytic current is increased by 221% with the vacancy-rich MoS₂ as electrocatalyst for hydrogen evolution reaction (HER). A small overpotential of 75 mV is needed to deliver a current density of 10 mA cm⁻², which is considered among the best values achieved for MoS₂. It is envisaged that this work may provide a new strategy for utilizing the semimetal phase for structuring MoS₂ into a multi-functional material.

1. Introduction

The elemental vacancies in materials, which are generally called defects, are actually considered to be perfect and powerful tools for designing various functional materials [1–4]. The vacancies can be viewed as virtual atoms that have an empty electronic state at the vacuum level, and thus the charge imbalances will lead to the redistribution of charges and consequently induce defect levels in the band gap, resulting in a richness of phenomena such as band gap narrowing, band bending, and symmetry distortion [5–7]. As a typical two-dimensional (2D) material, MoS₂ provides an ideal prototype to explore the interaction between vacancies and functions, especially in the field of electrochemical water splitting [8–13]. It has been clearly proven that the edge sites are catalytically active, while the basal plane is pretty inert [14]. Recent work demonstrated that sulfur vacancies could serve as another important catalytically active site for HER due to the favorable adsorption free energy [15,16]. This is supported by the

theoretical calculations of the formation energy of S vacancies, which is much lower than that of Mo vacancies. The major result is the emergence of impurity states in the bandgap that allow favorable hydrogen adsorption [17–19].

However, the controlled fabrication of S vacancies in the inert plane of MoS₂ is a formidable challenge and generally needs critical conditions such as electron/argon irradiation, hydrogen plasma treatment, or high temperature annealing [20,21]. A recent work reported the possibility of creating S vacancies in the electrochemical process but need a large accessible applied potential. This is understandable because removal of S by H₂ to release H₂S is very endothermic and kinetically difficult to achieve [22,23]. Recent work found that the robust electronic states on topological insulators could enhance the adsorption of various molecular species when covered by selected catalytic metal layers [24]. Informed by the deposition of oxide thin films on the substrate, where oxygen vacancies can be formed due to the strong affinity between oxygen and the element from the substrate [25], it is

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very interesting to explore the synergistic effect on the formation of S vacancies in the semimetal phase – supported MoS₂.

As a recent defined semimetal, CoMoP₂ is selected as the supporting substrate because of the good conductivity and similar hexagonal structure as MoS₂ [26]. Density functional theory (DFT) calculation predicted that the S atoms in the basal plane could be activated and removed by bonding with hydrogen. The formation energy barrier for H₂S was significantly decreased in comparison with the pure MoS₂ phase without support. S vacancies with a concentration of 13% could be created in the electrochemical process. Consequently, the catalytic current was increased by 221% at a given overpotential (−0.25 V vs RHE) and show high stability in a wide potential window. This opens new pathways for the ready creation of vacancies in 2D materials for various applications.

2. Experimental

2.1. Synthesis of the catalysts

The topological semimetal CoMoP₂ was synthesized by solid state reaction. In a typically synthesis, 0.25 mmol NH₄Mo₇O₂₄ · 4H₂O, 1.75 mmol Co(NO₃)₂·6H₂O, 4 mmol (NH₄)₂HPO₄, 4 mmol citric acid, and 2.5 g urea were dissolved in distilled water. Then solution was dried at 80 °C and then heated at 500 °C for 4 h in the air. After this, it was moved into a tube furnace and heated at 850 °C for 2 h with a heating rate of 1 °C/min. Hydrogen flow was used in this process.

For the synthesis of MoS₂/CoMoP₂ heterostructure (CMPS), 50 mg of the as-synthesized powder, 50 mg of (NH₄)₂MoS₄, and a Ni foam were placed in a 50 mL autoclave filled with 20 mL of *N,N*-Dimethylformamide. 0.1 mL of N₂H₄ · H₂O was added drop by drop. The mixed solution was transferred into an oven and heated at 180 °C for 24 h. The produced product was washed with water first and then with ethanol, and dried at 60 °C for the following characterization.

2.2. Characteristic techniques and electrochemical activation strategy

Powder X-ray diffraction (XRD) data were recorded with a Bruker D8 Advance diffractometer equipped with a Cu Kα source (λ = 0.15406 nm). The morphologies and structures of the products were characterized with TITAN 80/300 electron microscope. XPS investigation was carried on a UHV surface analysis system equipped with a Scienta-200 hemispherical analyzer. The base pressure of a sample analysis chamber is 2 × 10^{−10} mbar.

Electrochemical activation and performance assessment were performed on the Autolab PGSTAT302N with impedance module electrochemistry workstation. A conventional three electrode cell configuration was employed. The Ni foam with pristine CMPS sample were used directly as working electrode. A Ag/AgCl (3 M KCl) electrode was used as the reference electrode, and a graphite rod was used as the counter electrode. 1 M KOH was used as electrolyte. Linear sweep voltammetry was recorded at a scan rate of 1 mV/s. All the polarization curves were iR-corrected by electrochemical impedance spectroscopy (EIS). The solution resistance (R_s) was estimated from the impedance at high frequency (|Z(jω)|ω → ∞). The activation process was performed in potentiostatic mode at −0.126 V vs RHE for 40 h. All the potentials reported in this work were converted to a reversible hydrogen electrode according to $E \text{ (versus RHE)} = E \text{ (versus Ag/AgCl)} + (0.207 + 0.059 \text{ pH}) \text{ V}$.

2.3. Theoretical calculations

The crystal structure of CoMoP₂ is fully relaxed (including the shape and the volume of the unit cell, and the internal positional parameters), and the optimized lattice parameters agree well with experimental values within a discrepancy of 0.5%. The optimized lattice parameters of CoMoP₂ in a–b plane were used to construct the basic unit of the

supercell in a–b plane. Taking account of the necessity of creating S vacancies in supercells and the acceptable computational efforts of DFT methods when treating vacancies in solids, in a–b plane, the dimension of the supercell is chosen to be 4×4 basic units of CoMoP₂. The heterostructure is constructed by adding one monolayer of 2H-MoS₂ on top of the Co-terminated CoMoP₂ (001) surface. All calculations on supercells in this work are based on the slab model, and the thickness of the vacuum region is chosen to be as large as 12 Å in order to reduce the mirror image effect to a negligible value. In this work, we keep the shape and the volume of supercells fixed, optimize the internal positional parameters of supercells only, and keep the Co atomic layer at the bottom of each supercell fixed mimicking the CoMoP₂ substrate.

3. Results and discussions

3.1. Theoretical prediction of S vacancy formation

To explore why and how S vacancies are formed, we first performed DFT calculations of the surface free energies on three different supercells: (a) In the case with one S atom adsorbed on the S vacancy (denoted as □S, which can also be called pristine MoS₂/CoMoP₂ heterostructure (CMPS), as shown in Fig. S1a); (b) In the case with one S vacancy (denoted as Mo□S_x/CoMoP₂, as shown in Fig. S1b), and (c) For the case with one H adsorbed on the S vacancy (denoted as Mo□S_x(H)/CoMoP₂, as shown in Fig. S1c). As shown in Fig. 1b, the surface energy of Mo□S_x/CoMoP₂ is larger than that of pristine structure, until the potential of as low as −1.26 V vs RHE. This is inconsistent with previous research, which indicated that in spite of perfect 2D materials such as MoS₂, being predicted to be unstable upon thermal fluctuation [27], the creation of vacancies in the basal plane is reasonably difficult [28]. However, once created, they can be occupied immediately by hydrogen atoms under the electrochemical conditions in a broad potential window below 0.42 V vs RHE as illustrated by the arrow in Fig. 1b. This value is much higher than that of pure MoS₂ phase, with a value of −0.26 V vs RHE [22]. This readily explains the instability of S vacancies because they can be easily passivated by adsorbates [29]. Obviously, the vacancies created while supported on semimetal CoMoP₂ are more stable than the pure MoS₂ phase. We then calculated the Gibbs free energy for H₂S, which is the desulfurization process of making S vacancies. This is a two proton-electron transfer process, as shown in Fig. 1a and b. The transfer of the first electron and proton needs an energy of 1.43 eV, while the second protonation to form adsorbed H₂S is uphill by about 1.51 eV from the first step. However, the whole reaction becomes exergonic with an absolute applied potential in the electrochemical environment. The ΔG for formation of gaseous H₂S was decreased to only 0.08 eV for the MoS₂/CoMoP₂ heterostructure, which is much lower than that for pure MoS₂ with a value of −0.83 eV. This means that the S can be removed more efficiently as H₂S gas and serves as activity centers in the following HER process.

3.2. Catalyst structure and composition

Based on the calculations, we constructed the hybrid structure by a two-step process as illustrated in Fig. 1d. CoMoP₂ nanoparticles were synthesized first by the in-situ reduction of Co-Mo complex precursor at high temperature under H₂ flow. Then, the pristine MoS₂ was directly grown on a Ni foam in the solution containing CoMoP₂ nanoparticles and ammonium thiomolybdate ((NH₄)₂MoS₄). As revealed in the X-ray diffraction pattern (Fig. 2a), the main peaks can be assigned to the hexagonal phase of CoMoP₂ with a space group *P*6₃/*mmc*, No.194 (*a* = 0.333 nm, *c* = 1.122 nm). The absence of diffraction peaks of MoS₂ prove that the obtained pristine phase is amorphous. Fig. 2b shows the Scanning electron microscope (SEM) image of the final structure, with MoS₂/CoMoP₂ particles grown on the Ni foam. The corresponding energy-dispersive X-ray spectroscopy (EDS) analysis confirmed the particle is composed of the elements Mo, S, Co, and P

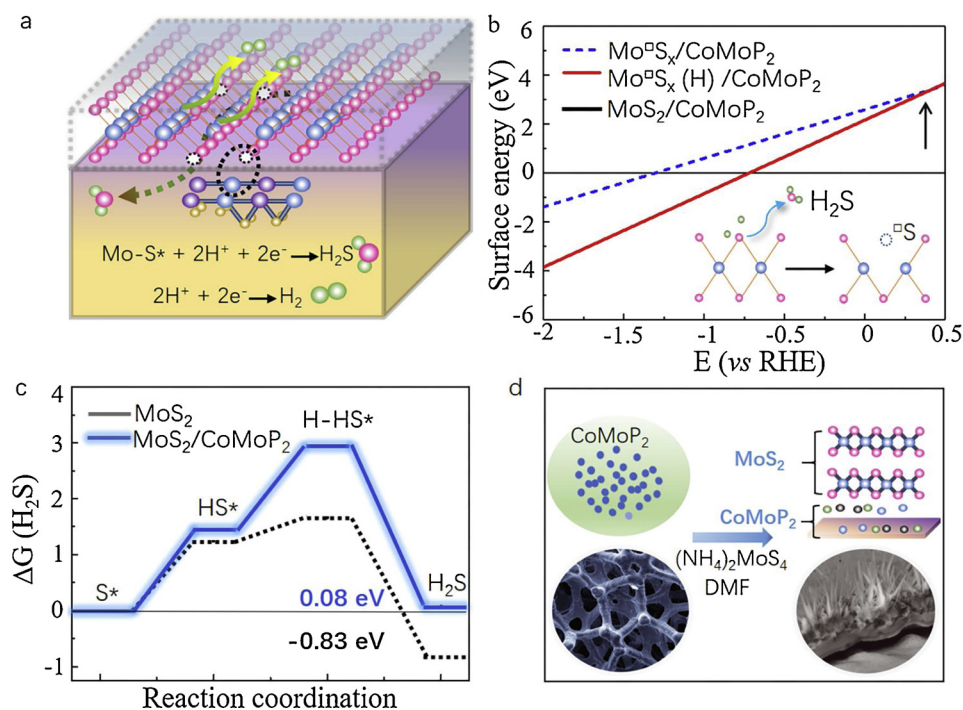


Fig. 1. (a). Illustration of the creation of S vacancies in the basal plane of MoS₂. S is removed with a two-step process in the form of H₂S. The created S vacancies can serve as active sites for HER. (b). The calculated surface free energy of pristine MoS₂/CoMoP₂ (Black line), MoS₂/CoMoP₂ with S vacancies (Mo[□]S_x/CoMoP₂), and with a hydrogen adsorbed on the S vacancy (Mo[□]S_x(H)/CoMoP₂). (c). Comparison of the Gibbs free energy for the formation of H₂S between MoS₂/CoMoP₂ and pure phase of MoS₂. (d). The syntactic strategy for the semimetal supported MoS₂.

(Fig. 2b), which were distributed homogeneously according to elemental mapping (Fig. S2). High-resolution transmission electron microscopy (HRTEM) further confirmed the crystallinity and composition of the as-synthesized hybrid structure. Several nanoparticles are covered by a thick layer of amorphous shell (Fig. 2c), but one can observe some tiny layered structures at the edge with a lattice fringe spacing of ~0.6 nm, corresponding to the (002) facet of bulk 2H-MoS₂ (Fig. 2d), indicating the formation of a few crystalline nuclei from the amorphous matrix [30]. The lattice-resolved image of a single crystalline domain embedded in the amorphous matrix has an interplanar spacing of 0.19 nm, which corresponds to the (114) plane of hexagonal CoMoP₂

phase (Fig. 2e). This is consistent with the fast-Fourier transform (FFT) image that recorded along the [221] direction (Fig. 2f).

3.3. Electrochemical activation and HER performance

The electrochemical activation process of the pristine MoS₂ for HER was conducted in 1 M KOH solution in a standard three-electrode electrochemical cell. All the LSV curves displayed in this work are corrected to remove the iR drop by electrochemical impedance spectroscopy (EIS). At the current density of 10 mA/cm², Pt/C and bare Ni foam exhibited HER overpotentials of 26 mV and 200 mV, respectively

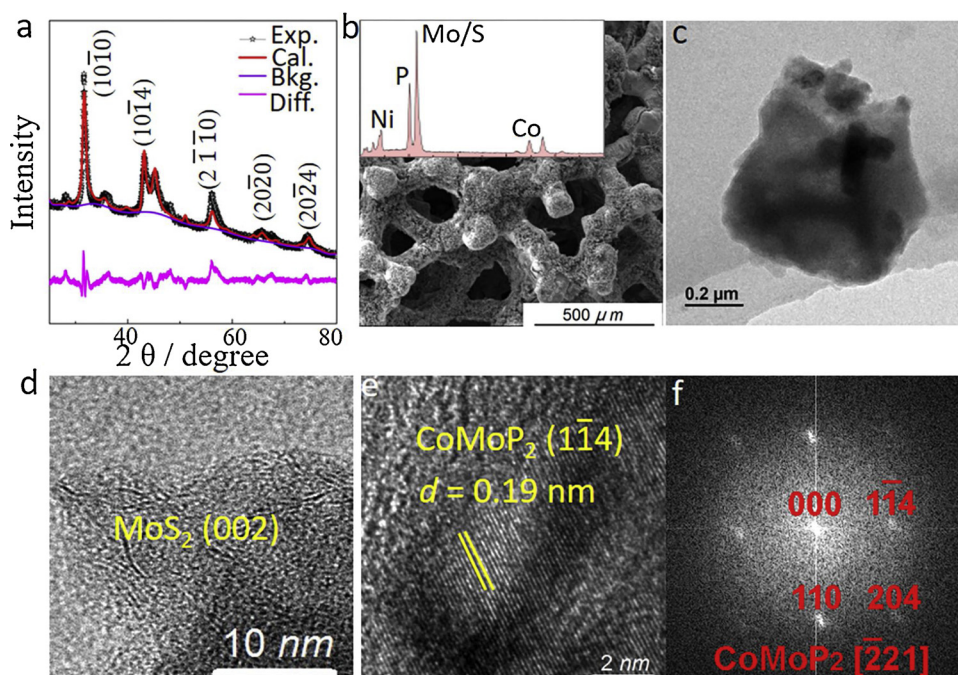


Fig. 2. (a). The XRD pattern of the synthesized MoS₂/CoMoP₂ sample. (b). SEM and (c). TEM image of the MoS₂/CoMoP₂ particle. (d). HRTEM shows the low crystalline MoS₂ phase outside, and (e). Semimetal CoMoP₂ phase inside, and (f). The corresponding fast Fourier transform (FFT).

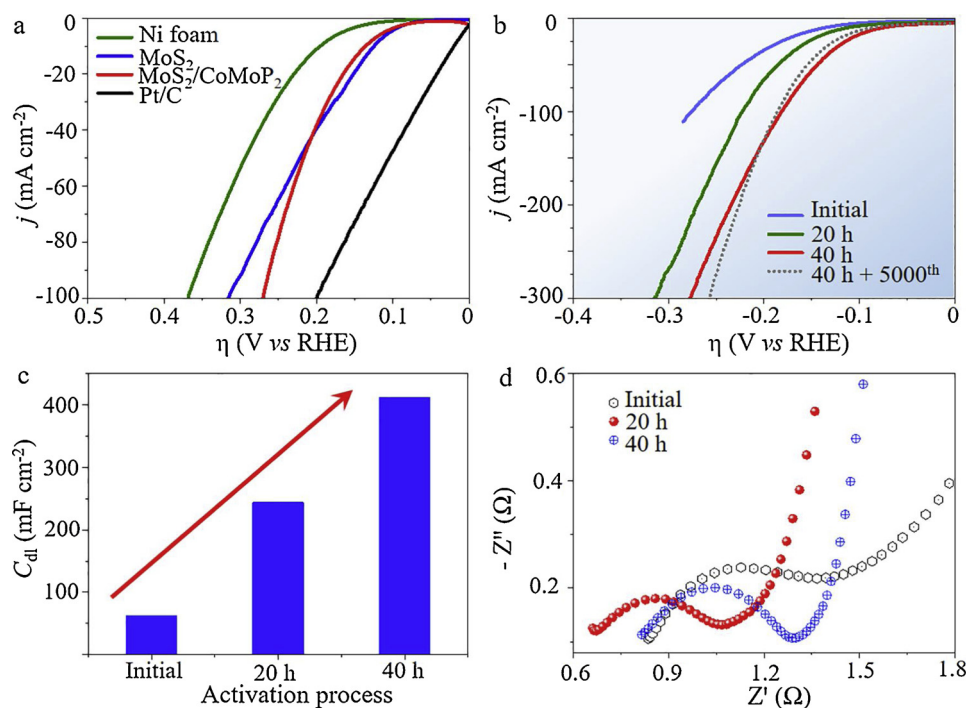


Fig. 3. (a). Polarization curves of Ni foam (NF), pure MoS₂ phase, commercial Pt/C catalyst, and pristine MoS₂/CoMoP₂. (b). Comparison of polarization curves for the MoS₂/CoMoP₂ catalyst in the initial test, and after activation for 20 h, 40 h, and 40 h plus 5000 cycles. (c). Plot showing the increase of double-layer capacitance (C_{dl}) for the pristine and vacancy-rich MoS₂/CoMoP₂ sample for the initial test, activated for 20 h, and 40 h, respectively. (d). Impedance measurement of the pristine MoS₂/CoMoP₂ and activated for 20 and 40 h, respectively.

(Fig. 3a). The HER activity of the pure MoS₂ and pristine CMPS are roughly the same, which is 116 and 126 mV, respectively. Furthermore, the linear parts of the polarization curves were fitted by the Tafel equation, yielding Tafel slopes of 30, 109, 67, and 80 mV/dec. for commercial Pt/C, Ni foam, bare MoS₂, and pristine CMPS samples, respectively (Fig. S3). These results indicate that the pure MoS₂ and pristine CMPS have the similar HER activities during the initial measurements. Then, a long-term stability test was carried out on the pristine CMPS sample with a constant overpotential of 126 mV without iR corrections (Fig. S4). Interestingly, instead of remaining unchanged or exhibiting degradation in current densities with increasing measurement time, we found a continuously increasing current density. The polarization curve was recorded after 20 h of measurement, as shown in Fig. 3b. The overpotential to deliver a current density of 10 mA/cm² is decreased to 110 mV. For a meaningful comparison, a normalized current density increment is defined as $\Delta j/J_0$, where J_0 is the current density of pristine CMPS, and Δj is the current density increase at -0.25 V [22]. This value was determined to be 115% after 20 h, and it increased to 221% after another 20 h of further testing. Impressively, the overpotential to produce a current density of 10 mA/cm² is only ~75 mV after activation. This value is better than most reported MoS₂ based catalysts (Table S1), such as CoS-doped β -Co(OH)₂@amorphous MoS_{2+x} hybrid (143 mV) [31], MoS₂/Ni₃S₂ heterostructures (110 mV) [32], MoS₂/NiCo-layered double hydroxide (78 mV) [33], and metallic-phase MoS₂ nanosheets (175 mV) [34]. Furthermore, the polarization curve after 40 h plus 5000 cycling test are compared in Fig. 3b. The minuscule difference in current density suggests a high long-term stability of our vacancy-rich catalyst in the HER process.

To confirm the increase of active centers, the active surface areas of the catalyst before and after activation were analyzed by their electrochemical double layer capacitances (C_{dl}) (Figs. S5–S7). As shown in 3a, the C_{dl} increased dramatically from 62.1 to 244 mF cm⁻² after 20 h activation, and finally to 412 mF cm⁻² after 40 h, illustrating that the increase in catalytic current can be attributed to the increased electrochemical surface area of MoS₂. Electrochemical impedance spectroscopy (EIS) was performed under the HER conditions (Fig. 3d). The EIS plots can be fitted excellent by two-time constant serial (2TS) model. The semicircle at high frequency (HF) can be assigned to the charge transfer kinetics from catalyst to adsorbates. The charge transfer

resistance is decreased from 4.8 Ω to 3.2 after 20 h activation, and further decreased to 2.6 Ω after 40 h. Bode phase diagram clearly reveals the relaxation time at HF as shown Fig. S8. After catalyst activation, the intensities of HF semicircle decrease and shift to higher frequencies, indicating an increase in the reaction rate and shorter reaction time constant ($\tau = 1/\omega_p$, where τ is the time constant and ω_p is the characteristic frequency). This indicates an increase in the number of edge-terminated states or vacancy states that were acting as catalytic centers, which favors electron injection in the HER process. Previous studies found that metal phosphides such as MoP and CoP are also excellent electrocatalysts for HER [35,36]. Thus, as a comparison, pure MoS₂, CoMoP₂, and Ni foam were tested further proving the activation process. The results showed a stable performance without activation from the LSV curves (Figs. S9–S11). All these suggest that the using of CoMoP₂ substrate is very important for the activation process.

Finally, we tried to investigate the HER behavior under acidic condition. Surprisingly, there was no obvious activation happened from the LSV curves (Fig. S12). This maybe caused by the presence of large number of protons in acidic solution. The Volmer process for HER has a smaller Gibbs free energy than that of S-vacancy formation. Thus, rather than the formation of H₂S gas, hydrogen atoms are reduced to forming hydrogen gas.

3.4. Catalyst structure evolution before and after electrochemical activation

The phase structure, as well as the formation of S vacancies were examined by X-ray photoelectron spectroscopy (XPS). For the pristine MoS₂/CoMoP₂ sample, a small S 2s peak (226.1 eV) next to the Mo 3d_{5/2} peak was observed (Fig. 4a) [37,38]. Specifically, these doublets with binding energies of 228.6/231.9 eV can be assigned to the Mo 3d signal of Mo-P bonding in CoMoP₂ (Fig. 4a). The peaks located at 229.8 and 233.1 eV with a separation of 3.3 eV can be attributed to the Mo species in MoS₂ phase [39,40]. Moreover, the Mo 3d peaks at higher binding energies (232.5 eV and 235.7 eV) demonstrate slight surface oxidation of the pristine MoS₂ surface into MoO₃ [41]. The S 2p peak, on the other hand, can be best fitted with two doublets of S 2p_{3/2} energy states (Fig. 4b). The binding energy of 161.5 eV corresponds to the terminal (edge) site of S²⁻ species, which have been identified clearly as active sites for the HER catalytic activity in MoS₂ [15]. The higher binding

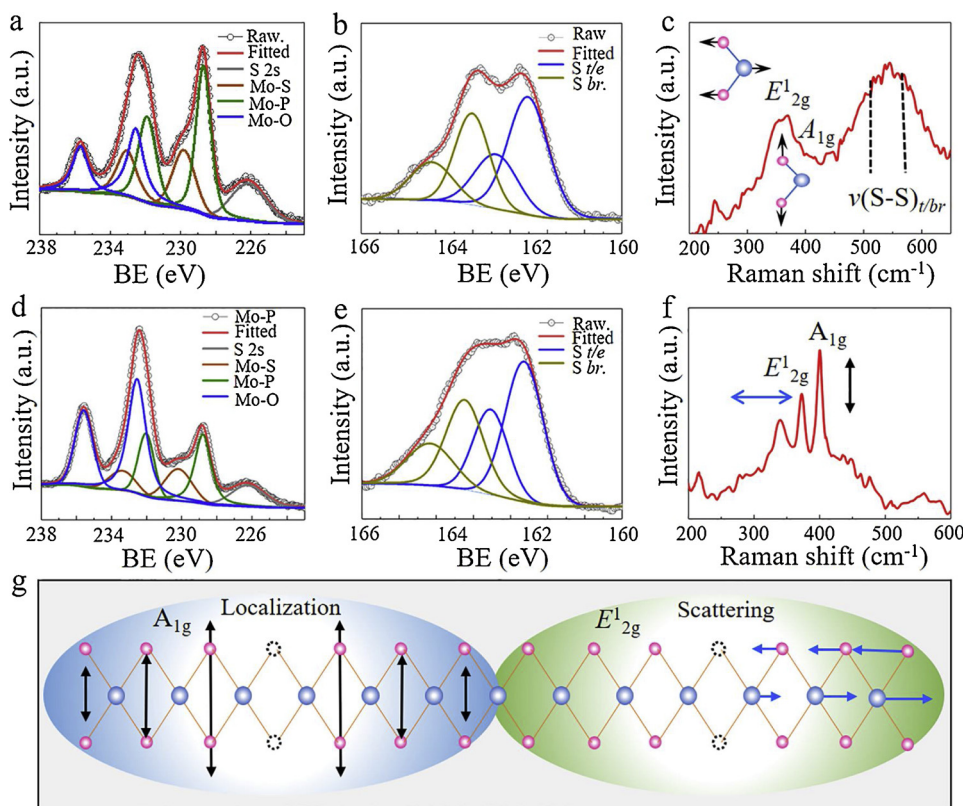


Fig. 4. (a). XPS spectra of Mo 3d peak, and (b). S 2p peak, for the pristine MoS₂/CoMoP₂ sample. (c). Raman spectrum of the pristine MoS₂/CoMoP₂. XPS spectra of (d). Mo 3d peak, and (e). S 2p peak, for the activated MoS₂/CoMoP₂ sample. (f). Raman spectrum of the MoS₂/CoMoP₂ after activation. (g). An illustration of the function of S vacancies as localization and scattering centers for Raman vibration.

energy at 163 eV can be assigned to the bridging disulfide S₂²⁻ ligand or apical S²⁻ ligand [42,43]. The atomic ratio between S and Mo is determined to be 2 by the above fitting results. Further insight into the pristine MoS₂ nanostructure was obtained by examination of Raman spectrum (Fig. 4c). The broad peak between 350–420 cm⁻¹ belongs to the E_{2g}¹ (in plane motion of Mo and S in opposite directions) and A_{1g} (out of plane motions of S atoms) vibrational modes of hexagonal MoS₂ phase, respectively. Of particular note is the dramatically decrease in the relative intensities of A_{1g} to E_{2g}¹ in comparison with the bulk phase, suggesting that the as-prepared MoS₂ structure is edge-poor [30,39]. This readily explains the poor initial HER activity as discussed below. Another broad peak centered at 543 cm⁻¹ is a feature of the amorphous MoS₂ phase, which can be assigned to the ν-(S-S)_{terminal} and ν-(S-S)_{bridging} vibrations [44,45].

In comparison with the pristine sample, the binding energies for Mo–O and Mo–P bonding remained unchanged (Fig. 4d) after activation. The increase in the peak density of Mo–O bonding (232.5 eV) can be explained by surface oxidation, as observed in other systems. Interestingly, the full width at half maximum of the Mo–S peak was larger than that of the pristine sample, and the binding energy shifted to a lower position by 0.11 eV. This means the element Mo has different S coordination and lower valence states should exist after activation. The investigation of S 2p spectra indicates that the intensity was significantly reduced after compared to the Mo 3d peak, while the relative intensity of terminal/edge S was increased by comparison with basal bridging component (Fig. 4e). The atomic ratio between S and Mo was decreased to 1.73 by fitting the spectra, corresponding to a S vacancy concentration of 13%. All these suggest the creation of S vacancies after activation, which serves as active centers for HER [46]. More evidence was provided by the Raman spectra, as shown in Fig. 4f. The strong A_{1g} peak reveals that the out of plane vibration is favored, suggests in the increasing of terminal/edge-terminated component [30,39]. The red shift of A_{1g} (401 cm⁻¹) to E_{2g}¹ (372 cm⁻¹) in comparison with the bulk phase was the result of increases in disorder associated with edge defects [47,48]. Additionally, a satellite peak was observed beside the E_{2g}¹

mode, sitting at smaller wavenumbers of 341 cm⁻¹. This further positively confirms that the defects are from S vacancies as expected from previous theoretical predications: the S vacancy could be the localization centers for out of plane vibration and strengthen the A_{1g} mode, while acting as scattering centers for in-plane vibration (E_{2g}¹ mode) and causing the atoms around the vacancies to have a smaller vibrational amplitude (Fig. 4g) [49,50].

4. Conclusions

In conclusion, large concentrations of S vacancies were created in the basal plane of MoS₂ when supported on the topological semimetal CoMoP₂. Structural characterization revealed that the created vacancies can serve as new catalytic centers for HER and are related to the increase in catalytic current by more than a factor of two, and the efficient electron injection from the electrode to the catalyst. DFT calculations further confirmed these results by revealing a significant decrease in the Gibbs free energy for H₂S in the electrochemical process. This synergistic approach could not only be used to design high performance HER catalysts, but also provides a general strategy to creating vacancies for various applications.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the

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